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REVIEW

Recent advances in 4-hydroxycoumarin chemistry. Part 2: Scaffolds for heterocycle molecular diversity

Moaz M. Abdou [a,d,*], **Rasha A. El-Saeed** [b], **Samir Bondock** [b,c]

[a] *Egyptian Petroleum Research Institute, Nasr City, P.O. 11727, Cairo, Egypt*
[b] *Department of Chemistry, Faculty of Science, Mansoura University, ET-35516 Mansoura, Egypt*
[c] *Department of Chemistry, Faculty of Science, King Khalid University, 9004 Abha, Saudi Arabia*
[d] *The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan*

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Annelated heterocycles;
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Green chemistry

Abstract The present paper aims to review the synthetic applicability of 4-hydroxycoumarin in heterocyclic synthesis during the period from 1996 up to now. This compound can be used as building blocks for five, six, and seven-membered heterocycles as well as fused rings.
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* Corresponding author. Tel.: +20 1000409279.
E-mail address: moaz.chem@gmail.com (M.M. Abdou).
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1. Introduction

4-Hydroxycoumarin is a well-known versatile synthon and important reagents in the realm of heterocyclic synthesis (Abdolmohammadi, 2014; Abdou et al., 2013; Aggarwal et al., 2013; Ahadi et al., 2014; Altieri et al., 2010; Azizi et al., 2014; Bakthadoss and Sivakumar, 2014; Chen et al., 2013; Darehkordi et al., 2014; Davarpanah and Kiasat, 2014; Eskandari et al., 2013; Ghosh and Khan, 2014; Golzar et al., 2013; Gu et al., 2009; Hossain et al., 2013; Hossaini et al., 2013; Jashari et al., 2014; Jin et al., 2013; Jung and Park, 2009; Lee et al., 2012; Mei et al., 2013; Metwally et al., 2013, 2012a, 2012b, 2012c, 2012d; Mungra et al., 2011; Nair et al., 2014; Nishino et al., 2014; Pal et al., 2013; Ponpandian and Muthusubramanian, 2014; Rad-Moghadam et al., 2014; Rajawat et al., 2014; Saha, 2013; Sato et al., 2013; Siddiqui and Khan, 2013, 2014; Xiao et al., 2014; Zhao and Du, 2014; Ziarani and Hajiabbasi, 2013). It is of particular interest as a very promising reagent for cascade heterocyclization, which will undoubtedly become one of the main approaches to the targeted synthesis of heterocycles in the near future, in the rapidly-rising field of combinatorial chemistry.

In a continuation of our research program aiming at the utilization of cyclic 1,3-diketone compounds as scaffolds for heterocycle molecular diversity (Abdou, 2017a, 2017b, 2017, 2018, 2017, 2013b, 2013c; Abdou et al., 2013, 2012), the first part of this review article (Abdou, 2019) is dealt with most recent advances in 4-hydroxycoumarin chemistry made since 1996 up to date and concentrates on synthesis, chemical reactivity and reactions of 4-hydroxycoumarin. The second part intends to illustrate the research efforts that occurred in the application of 4-hydroxycoumarin in heterocyclic synthesis covering the same period of time. The presence of reactive centers in this compound provides ample opportunities to synthesize a great variety of novel compounds under relatively mild conditions and using simple laboratory equipments. Thus, the two parts are complementary and display current trends in 4-hydroxycoumarin chemistry.

In this literature survey, the reactions involving 4-hydroxycoumarin occur with high regioselectivity and its course can easily be controlled by changing reaction conditions and varying substituents in the molecules of initial compounds. The heterocyclic compounds are obtained in a single step with high yield and they are reported in order of the increase of (i) the number of rings, (ii) the size of such rings and (iii) the number of heteroatoms present. The sequence of heteroatoms followed is: nitrogen, oxygen and sulfur. The site of fusion in fused heterocycles is indicated by the numbers and letters and the numbering of the heterocyclic ring systems is that reported by chemical abstracts.

2. Synthesis of monocyclic heterocyclic compounds

2.1. Synthesis of five-membered systems with two heteroatoms

2.1.1. Pyrazolin-5-ones

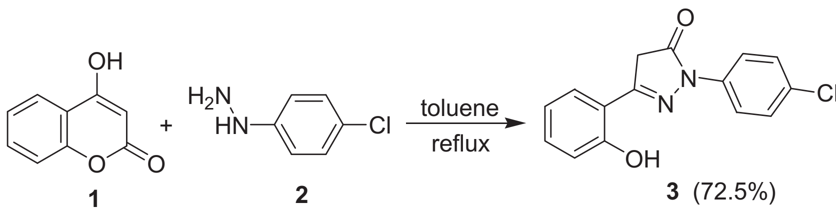
Froggett et al. (1997) described the reaction of 4-hydroxycoumarin **1** with a 1.5 equimolar excess of 4-chlorophenylhydrazine **2** in toluene under reflux, with azeotropic removal of water, furnished the 1-(4-chlorophenyl)-3-(2-hydroxy-phenyl)-2-pyrazolin-5-one **3** (Scheme 1).

The solvent-free reactions of substituted hydrazine hydrochlorides **4** with **1** in the presence of triethylamine were carried out by heating in the absence of solvent (90 min, 90–100 °C). In all cases, 1-aryl-3-(2-hydroxyphenyl)pyrazol-5-ones **6a-c** were formed along with the corresponding 4-(arylhydrazino) coumarins **5a-c** (Strakova et al., 2009) (Scheme 2).

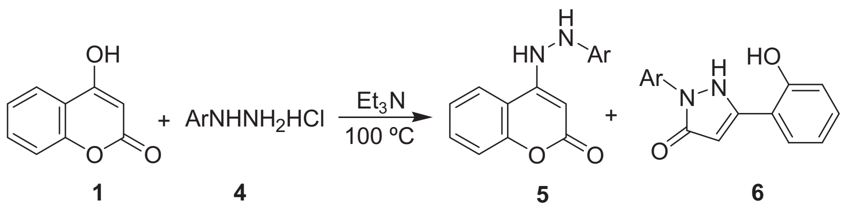
3-(2-Hydroxyphenyl)-1-methyl-1*H*-pyrazol-5-one **8** was obtained from the reaction of **1** with methylhydrazine **7** in ethanol. The reaction mixture was refluxed under N_2 flow (Zhao et al., 2010) (Scheme 3).

2.1.2. Imidazol-2(3H)-ones

The one-pot condensation of **1** with arylglyoxals **9** and ureas **10** in refluxing ethanol in the presence of a catalytic amount of acetic acid gave a colorless crystalline products that were identified as 4-aryl-5-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1*H*-imidazol-2(3*H*)-ones **11** (Kolos et al., 2009) (Scheme 4).

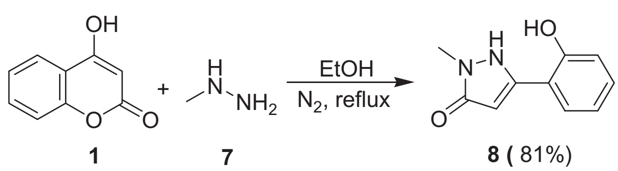


Scheme 1



4, 5, 6	a	b	c
Ar	Ph	4-Cl-C_6H_4	4-Br-C_6H_4
Yield % (**5/6**)	51/18	53/9	52/15

Scheme 2



Scheme 3

2.1.3. 1,2-Benzisoxazoles

Reaction of **1** with hydroxylamine hydrochloride in refluxing methanol represents one of the most successful strategies to attain 1,2-benzisoxazole-3-acetic acid **12**, which has been widely exploited because of their known important biological activities and application in different therapies (Lamani et al., 2009) (Scheme 5).

2.2. Synthesis of five-membered ring systems with more than two heteroatoms

2.2.1. Dithiazoles

The reaction of **1** with 4,5-dichloro-5*H*-1,2,3-dithiazolium chloride **13** in the presence of pyridine in dichloromethane at room temperature gave the corresponding 5-alkylidene-5*H*-4-chloro-l,2,3-dithiazoles **14** as a single stereoisomer in 87% yield (Jeon and Kim, 1999) (Scheme 6).

2.3. Synthesis of six-membered heterocycles containing one heteroatom

2.3.1. Quinoline

In 2010, a fast and solvent-free method was described for the synthesis of substituted quinoline derivatives *via* Friendländer synthesis is promoted, either under conventional heating or under MW irradiation, catalyzed by a derivatized silica bearing alkylsulfonic acid groups. The reaction of **1** with 2-aminobenzophenone **15** afforded 7-phenyl-6*H*-chromeno-[4,3-b]quinolin-6-one **16** and 2-(4-phenylquinolin-2-yl)phenol **17**. The addition of activated molecular–sieve powder to the reacting mixture increased the yield of **16** (40%) while dramatically reducing the yield of **17** (11%), *o*-hydroxy acetophenone **18** was the main product (about 50%) generated by the partial degradation of excess 4-hydroxycoumarin (Garella et al., 2010) (Scheme 7).

2.4. Synthesis of seven-membered heterocycles containing two heteroatoms

2.4.1. 1,4-Diazepines

It was reported that the condensation of **1** with *o*-phenylenediamine **19** in refluxing toluene (Hamdi et al., 2006) or under MW irradiation (Kidwai et al., 2005) afforded 4-(2-hydroxyphenyl)-2,3-dihydro-1*H*-1,5-benzo diazepin-2-one (Scheme 8).

3. Synthesis of fused heterocyclic compounds

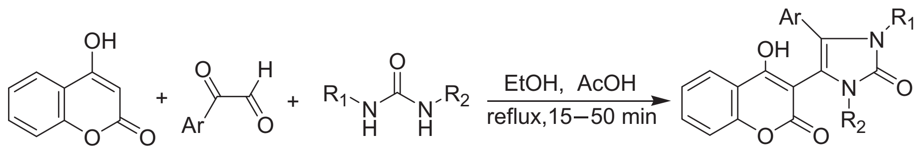
3.1. [5-6] Ring system

3.1.1. Pyrano[4,3-d]oxazol-4-ones

Ray and Paul (2004) published the one-pot synthesis of ben zo[1]pyrano[4,3-d]oxazol-4-one **22** consisting of the condensation of **1** with formamide **21** under reflux (Scheme 9).

3.1.2. Oxathiolo[5,4-c]-2H-chromen-4-ones

Reaction of 3-(chlorothio)-3-fluoro-2-(trifluoromethyl)-2-pro penoic acid methyl ester **23** with **1** leads to sulfenylation accompanied by cyclization giving rise to fused 2-(2,2,2-trifluoro-1-



1 9 10 11

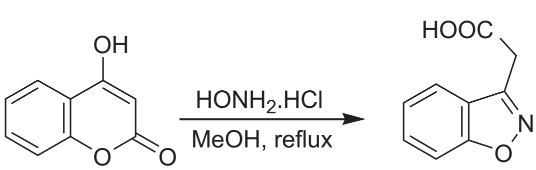
9,10	Ar	R_1	R_2	Yield%
a	Ph	H	H	70
b	4-Me-Ph	H	H	68
c	4-Cl-Ph	H	H	69
d	4-Br-Ph	H	H	63
e	4-I-Ph	H	H	63
f	Ph	Ph	H	69
g	4-Me-Ph	Ph	H	55
h	4-Cl-Ph	Ph	H	58
i	Ph	Me	Me	47
j	4-Me-Ph	Me	Me	45
k	4-Cl-Ph	Me	Me	45

Scheme 4

methoxycarbonylethylidene)-oxathiolo[4,5-c]-2*H*-chromen-4-one **24** (Kovregin et al., 2001) (Scheme 10).

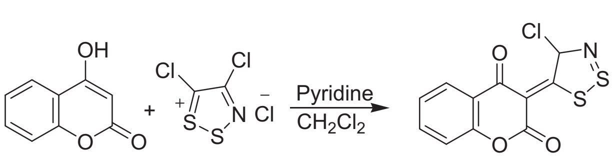
3.1.3. Dihydrofuran and furocoumarins

Furocoumarins are an important class of heterocyclic compounds possessing anticoagulant, insecticide, anthelminthic, hypnotic, antifungal, and HIV protease inhibition activities (Baichurin et al., 2013; Karami et al., 2013; Khan et al., 2013).



1 **12** (73%)

Scheme 5



1 13 **14** (87%)

Scheme 6

3.1.3.1. Oxidative cycloaddition reaction mediated by metal salts. The oxidative addition reaction of carbon-centered radicals to alkenes mediated by metal salts Ag (I), Ce (IV), Yb (III), Ru (II), and Mg(II) has received considerable attention over the last decade in organic synthesis for construction of carbon–carbon bonds.

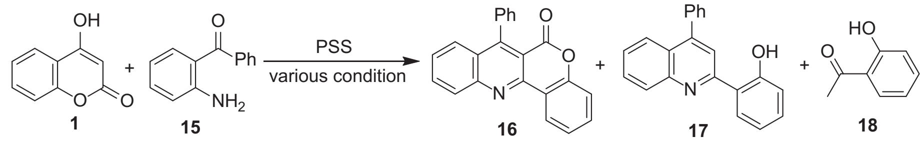
3.1.3.1.1. Using Ag (I). Lee and Kim (1997) have reported a facile and simple method for the synthesis of dihydrofurans, by the addition of silver (I)/Celite to the mixture of **1** and with ethyl vinyl ether **25** in acetonitrile under reflux (Scheme 11).

In a similar manner, medium- and large-sized ring substituted furans **28** could be also achieved *via* cycloaddition of **1** with a variety of vinyl sulfides **27** in refluxing acetonitrile (Lee and Kim, 1997) (Scheme 12).

3.1.3.1.2. Using Ce(IV). An efficient method for one-step synthesis of substituted 2-arylfurans has been developed by ceric (IV) ammonium nitrate (CAN) mediated oxidative cycloaddition of **1** with phenylacetylene **29** at 0 °C in acetonitrile giving linear and angular furocoumarin derivatives **30** and **31** as a mixture of regioisomers in good yields (Lee et al., 1998) (Scheme 13).

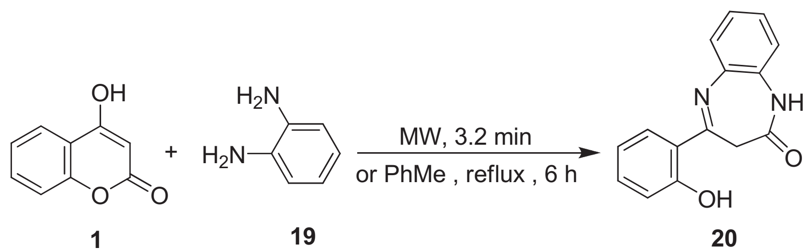
Lee et al. (2000) has also found that CAN(IV) was the much superior reagent for this oxidative cycloaddition than $Mn(OAc)_3.2H_2O$ and Ag_2CO_3/Celite. The reaction was typically carried out at 80 °C starting from **1** with methyl methacrylate **32** in the presence of CAN and excess amounts of sodium bicarbonate in acetonitrile giving the sole biologically interesting dihydrofurocoumarin **33** in 35% yield (Scheme 14).

Appendino et al. (1998) showed that treatment of **1** with 3-buten-2-ol and cerium (IV) ammonium nitrate (CAN) in



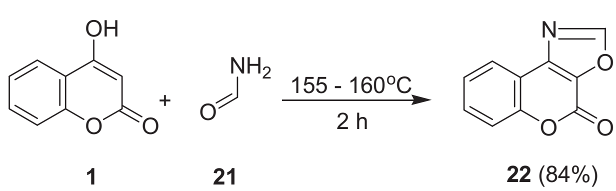
	Condition	time /min.	Yield % (16/17/18)
a	Conventional heating	60	13/20/---
b	80 °C, MW irradiation	5	22/36/---
c	80 °C, MW irradiation, Molecular sieve	5	40/11/50

Scheme 7

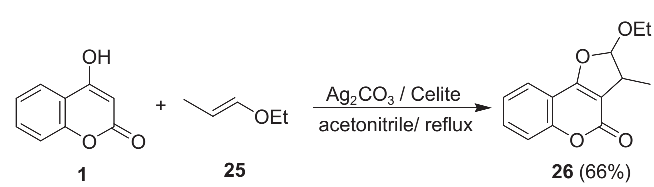


	Condition	Yield %
a	PhMe , reflux	80
b	MW	89

Scheme 8



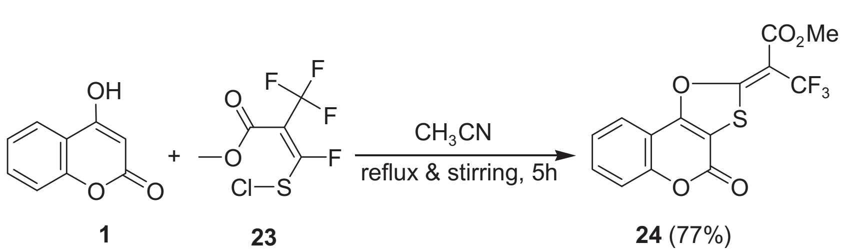
Scheme 9



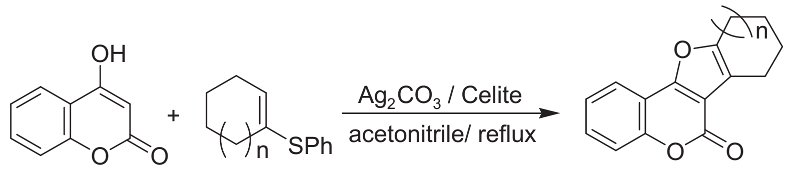
Scheme 11

acetonitrile at room temperature give a mixture of diastereomers **35** and **36** (Scheme 15). No substantial improvement of the ratio between angular and linear adducts could be achieved by changing solvent or metal oxidant and varying the temperature (Scheme 15).

It was also reported that the reaction of **1** with a range of alkenes in acetonitrile containing cerium (IV) ammonium nitrate (CAN) afforded the corresponding furo[3,2-c]pyranones **38** and furo[2,3-b]pyranone derivatives **39**. It should be noted that the reactions of **1** with vinyl benzoate and methylstyrene produced exclusively the furo[3,2-c]benzopyranone derivatives, as the sole isolated product; no more than a trace amount of the corresponding furo[2,3-b]benzopyranone derivatives was obtained in each of these



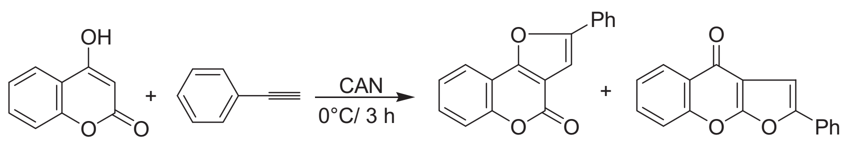
Scheme 10



1 **27** **28**

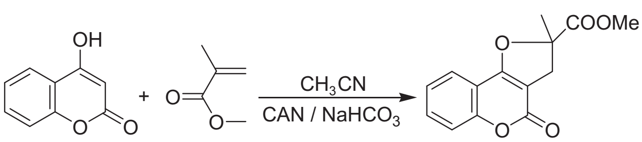
27, 28	a	b	c
n	1	2	3
Yield %	50	71	61

Scheme 12



1 **29** **30** (46%) **31** (16%)

Scheme 13



1 **32** **33** (35%)

Scheme 14

reactions, while formation of both the furopyranone derivatives was observed using other alkenes (Kobayashi et al., 1999) (Scheme 16).

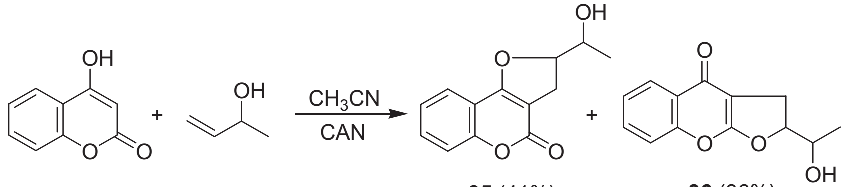
There has been a considerable interest in the use of CAN oxidation reactions in ionic liquids. Hence, reaction of **1** with methylstyrene **40** and CAN in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]-dichloromethane(1:9), gave tricycle **41** in 70% yield after 3 h. The CAN reaction in [bmim][BF_4]-dichloromethane (40 °C) is therefore more efficient and/or faster than reactions (at r.t. or at 40 °C) in acetonitrile. One further and important advantage to the use of [bmim][BF_4] is that on workup, the cerium byproducts form a precipitate at the end of the reaction (Bar et al., 2003) (Scheme 17).

3.1.3.1.3. Ruthenium(II). Cadierno et al. (2008) developed a simple strategy for the synthesis of multi-substituted furocoumarins by using a catalytic system consisting of the 16-electron allyl-ruthenium(II) complex [Ru(η3-2-C_3H_4Me)(CO)(dppf)][SbF_6](dppf = 1,1′-bis(diphenylphosphino)ferrocene) and trifluoro acetic acid (TFA) has been used to promote the coupling between secondary propargylic alcohol **42** and **1** to give 3-(4-methoxyphenyl)-2-methyl-furo[3,2-c]chromen-4-one **43** (Scheme 18).

3.1.3.1.4. Manganese(III) acetate. Yilmaz et al. (2008) have obtained 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-ones **45** from the radical cyclization of **1** mediated by manganese(III) acetate with electron rich alkenes **44** in 36–86% yields (Scheme 19).

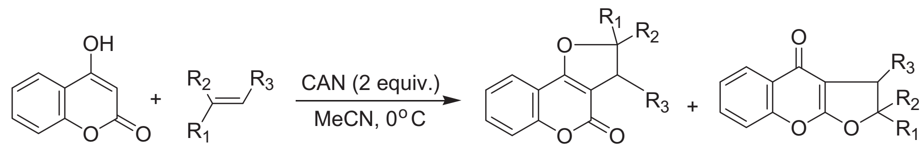
3.1.3.1.5. Multicopper oxidases (Laccases). Laccase (Agaricus bisporus)-catalyzed domino reaction of **1** with catechols **46** using atmospheric oxygen as the oxidant delivers for the synthesis of 10-substituted 8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-ones **47** as single regioisomers with yields of 61–99% (Leutbecher et al., 2011, 2005) (Scheme 20). Some of these compounds have been made accessible by crude peroxidase from onion solid waste (Angeleska et al., 2013).

3.1.3.2. [4+1] Cycloaddition reaction followed by a [1,3]-H shift. A [1+4] approach was developed by Majumdar et al. to prepare 3-hydroxy-2,3-dihydrofuro[3,2-c][1]benzopyran-4-one **49** through the reaction of **1** with chloroacetaldehyde **48** in the presence of aq. potassium carbonate at room temperature for 1.5 h (Majumdar and Bhattacharyya, 1997) (Scheme 21).



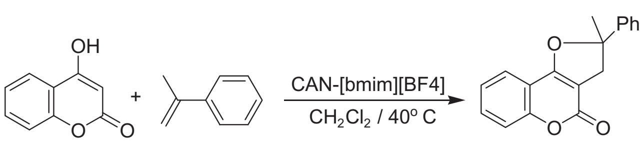
1 **34** **35** (41%) **36** (36%)

Scheme 15



37,38,39	R_1	R_2	R_3	Yield% (38/39)
a	CH_3	CH_3	CH_3	25/45
b	H	$(CH_2)_3$	$(CH_2)_3$	31/31
c	OAc	H	H	17/8
d	OBz	H	H	15/---
e	Ph	CH_3	H	62/---

Scheme 16



Scheme 17

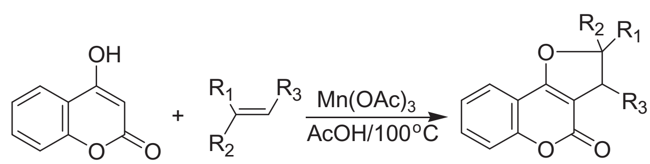
In a similar manner, Bondock et al. (2011) reported that antimicrobial active 2-(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole-4-yl)-4-*H*-furo[3,2-c]chromen-4-one was obtained via treatment of 2-chloro-1-(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)ethanone **50** with **1** in sodium ethoxide solution (Scheme 22).

2,3-Dihydro-2-hydroxy-3-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)furo[3,2-c]chromen-4-one **53** could be successfully prepared through the reaction of **1** with a 40% aqueous solution of glyoxal **52** in acetonitrile under reflux (Lamani et al., 2009) (Scheme 23).

Interaction of **1** with bromonitroalkenes **54** in aqueous sodium acetate and tetrabutylammonium bromide (TBAB) gave 2,3-dihydrofuro[3,2-c]chromen-4-ones **55** (Xie et al., 2011) (Scheme 24).

3.1.3.3. Multicomponent reactions.

3.1.3.3.1. Using of conventional synthesis. Several reports on the synthesis of furocoumarins *via* the multicomponent reactions of **1** with various arylaldehydes **56** and isocyanide **57** have been published during the last decade. In most of the

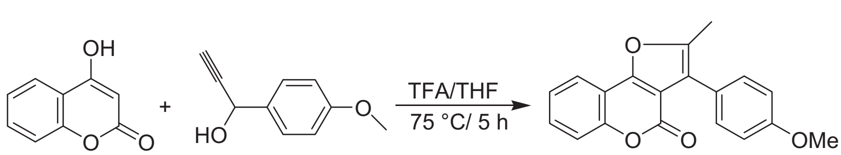


44,45	R_1	R_2	R_3	Yield %
a	Ph	H	Me	50
b	Me	Ph	H	81
c	Ph	Ph	Et	86
d	Ph	C_3H_7	Ph	36
e	Me	$OCOCH_3$	H	54

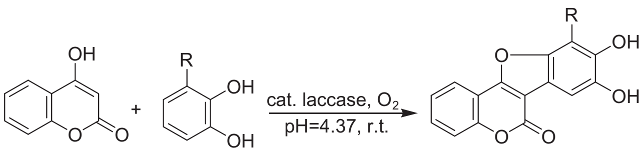
Scheme 19

cases, the yields of the desired furocoumarins **58** were moderate. Moreover, extended reaction times of up to 24 h under reflux conditions in toxic solvents such as benzene or toluene (Nair et al., 2002; Panja et al., 2012; Zhu et al., 2011) were required. These drawbacks restrictedly limit the applications for furocoumarin library construction (Scheme 25).

Consequently, there is need to develop a simple, rapid, eco-friendly and easy experimental and products' isolation procedure for the synthesis of these compounds.



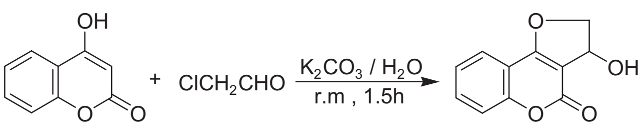
Scheme 18



1 46 47

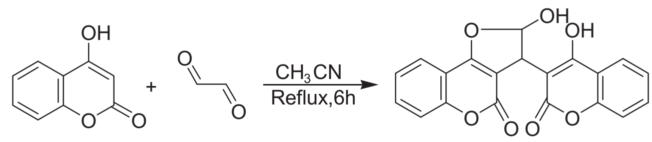
46,47	R	t/h	Yield %
a	H	7	85
b	Me	3	99
c	OMe	5	61
d	CO_2Me	4	89

Scheme 20



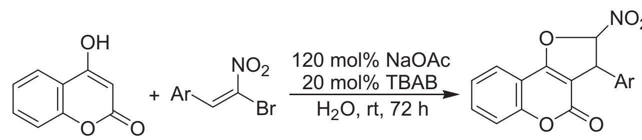
1 48 **49** (73%)

Scheme 21



1 52 **53** (73.6%)

Scheme 23



1 54 55

54,55	Ar	Yield%
a	4-MeO-C_6H_4	93
b	4-Me-C_6H_4	87
c	Ph	90
e	4-Cl-C_6H_4	96
f	4-Br-C_6H_4	83

Scheme 24

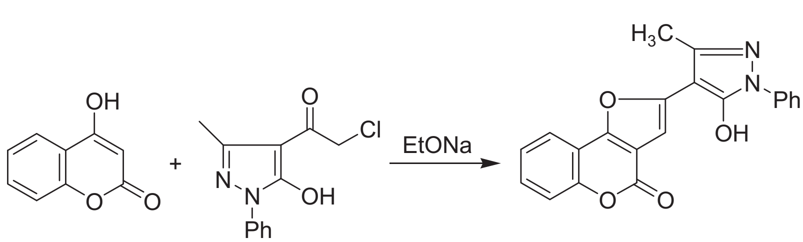
3.1.3.3.2. Using of microwave irradiation. Microwaves accelerated the synthesis of a range of furo[3,2-c]chromen-4-ones **59** *via* a three-component reaction of **1**, arylaldehyde **56** and cyclohexyl isocyanide **57** (Shaabani and Teimouri, 2003; Wu, 2006). By applying a microwave protocol (DMF, 150 °C, 5 min), reduction in reaction times (24 h → 3–5 min), higher yields and less by-products were observed compared to the conventional synthesis (Scheme 26).

3.1.3.3.3. Using of water. In fact, choice of solvent is one of the problems to face in order to perform eco-efficient processes. The presence of water was proven to be determinate for the success achieved by Shaabani et al. (2004). Further reasons that make water unique compared to other organic solvents are that it is cheap, not inflammable, and more important, it is not toxic. The environment-friendly one-pot three-component condensation reactions of **1**, *p*-substituted benzaldehyde **56**, and alkyl or aryl isocyanides **57** in water afforded furocoumarins **59** in good yields (Shaabani et al., 2004) (Scheme 27).

3.1.3.3.4. Using of solvent-free synthesis. Adib et al. (2009) have devoted considerable attention to an efficient and direct solvent-free synthesis of bioactive furo[3,2-c]chromenes *via* a one-pot and solvent-free reaction. Thus a mixture of **1**, aldehyde **56**, and isocyanide **57** underwent a one-pot addition reaction under an argon atmosphere and solvent-free conditions. The reaction proceeded at 180 °C and was complete within 1.5 h to produce *N*-alkyl-3-arylfuro[3,2-c]chromenes **59** in 91–95% yields (Scheme 28).

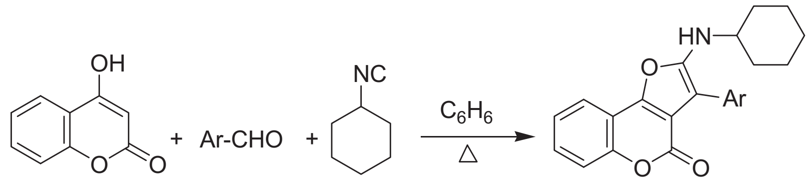
3.1.3.3.5. Using combination of solvent-free supported reagents and microwave. Shaabani et al. (2005b) have shown the combination of solvent-free supported reagents and microwave in the absence of solid supports and classical heating. One-pot method simply involves microwave irradiation of a mixture of *p*-substituted benzaldehyde **59** and **1** with isocyanides **60** in the presence of montmorillonite K10 to afford the corresponding products **61**. The reaction is completed in all cases within 4–5 min. Also, in this approach the use of large volume of benzene or toluene is avoided, work-up considerably simplified, and safety is increased by reducing the risk of over pressure and explosions (Scheme 29).

3.1.3.4. Using of electrochemical routes. One of the most successful strategies for the synthesis of 6*H*-benzofuro[3,2-c][1]ben



1 50 **51** (80 %)

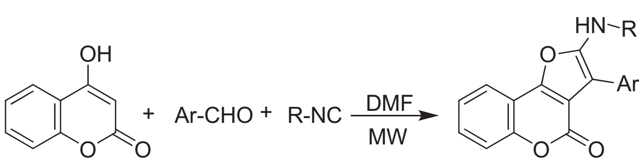
Scheme 22



1 56 57 58

56,58	Ar	t / h	Yield%
a	2-NO_2-Ph	24	69
b	4-NO_2-Ph	16	93
c	4-Cl-Ph	24	61
e	-Ph	24	77
f	4-MeO-Ph	16	62
g	4-Me-Ph	24	72

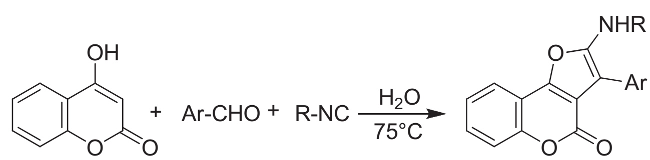
Scheme 25



1 56 57 59

56,57,59	Ar	R	Yield%
a	4-NO_2-Ph	*t*-Bu	84
b	4-NO_2-Ph	cyclohexyl	94
c	4-NO_2-Ph	2, 6-$(CH_3)_2$-Ph	92
d	4-Cl-Ph	cyclohexyl	85
e	4-MeO-Ph	cyclohexyl	90

Scheme 26



1 56 57 59

56,57,59	Ar	R	Yield%
a	4-NO_2-Ph	t-Bu	79
b	4-NO_2-Ph	c-Hex	85
c	4-NO_2-Ph	2, 6-$(CH_3)_2$-Ph	91
d	4-Cl-Ph	c-Hex	78
e	4-MeO-Ph	c-Hex	71

Scheme 27

zopyran-6-one derivatives **61** is electrochemical routes. Nematollahi et al. demonstrated the electrochemical oxidation of catechol (**60**a), 3-methylcatechol (**60**b), 3-methoxycatechol (**60**c), 2,3-dihydroxybenzoic acid (**60**d) and 3,4-dihydroxybenzoic acid (**60**f) with **1** as a nucleophile in the presence of potassium ferricyanide as an oxidizing agent in aqueous solution (Nematollahi et al., 2005; Golabi and Nematollahi, 1997a, 1997b) (Scheme 30).

3.2. Fused [6-6]ring system

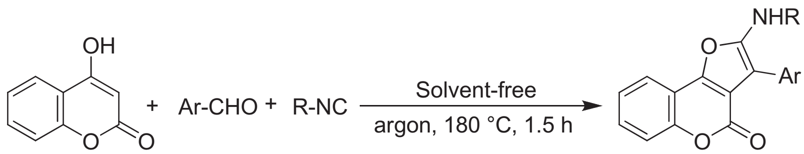
3.2.1. Benzopyrano[2,3-b]pyridine

Bandyopadhyay et al. (2010) reported the one-pot synthesis of the 1-benzopyrano[2,3-b]pyridine moiety **63** *via* Knoevenagel condensation by heating an equimolar mixture of **1** and 2-(monosubstituted amino)chromone-3-carbaldehyde **62** in boiling ethanol containing a catalytic amount of pyridine (Scheme 31).

Maiti et al. (2010) described the one-pot reaction of 2-(*N*-cinnamyl-*N*-aryl)amino-4-oxo-4*H*-1-benzopyran-3-carbaldehydes **64** with **1** by heating in ethanol in the presence of a catalytic amount of pyridine afforded substituted 11-allyl-6,11-dihydro-6-(4-hydroxy-2-oxo-2*H*-1-benzopyran-3-yl)-1-benzopyrano[2,3-b]quinolin-5*H*-5-one **65** (Scheme 32).

3.2.2. Pyrido[3,2-c]coumarins

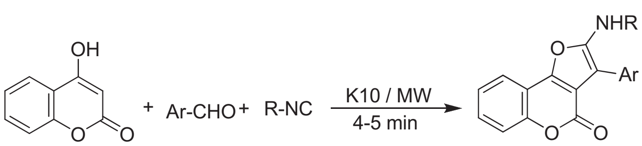
The work of Pandya et al. (2006) demonstrated that various diarylpyrido[3,2-c]coumarins **67** were synthesized in one step by reacting **1** with *α,β*-unsaturated ketones **66** in the presence of ammonium acetate and acetic acid (Scheme 33).



1 56 57 59

56,57,59	Ar	R	Yield%
a	Ph	c-Hex	91
b	Ph	t-Bu	95
c	4-MePh	t-Bu	95

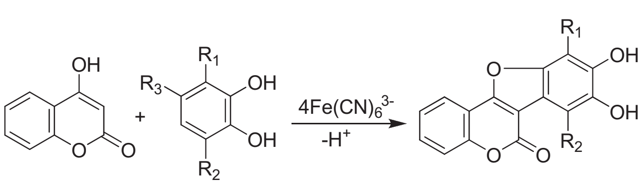
Scheme 28



1 56 57 59

56,57,59	Ar	R	Yield%
a	4-NO_2-Ph	t-Bu	72
b	4-NO_2-Ph	c-Hex	80
c	4-NO_2-Ph	2, 6-$(CH_3)_2$-Ph	70
d	4-Cl-Ph	c-Hex	72
e	4-MeO-Ph	c-Hex	74

Scheme 29



1 60 61

60,61	R_1	R_2	R_3	Yield %
a	H	H	H	96
b	CH_3	H	H	95
c	OCH_3	H	H	98
d	H	CO_2H	H	90
e	H	H	CO_2H	90

Scheme 30

3.2.3. *Chromeno[3,4-b][4,7]phenanthroline*

A short and environmental-friendly synthesis of chromeno[3,4-b][4,7]phenanthroline derivatives **70** was accomplished by three-component reactions involving an aromatic aldehyde **68**, 6-aminoquinoline **69** and **1** in water, under microwave irradiation without the use of any catalyst (Zhuang et al., 2008) (Scheme 34).

3.2.4. *Chromeno[4,3-b]benzo[f]quinolin-6-one*

Chromeno[4,3-b]benzo[f]quinolin-6-one derivatives **72** were obtained in good to high yields *via* the reaction of *N*-arylidenenaphthalen-2-amine **71** with **1** in aqueous media catalyzed by triethylbenzyl ammonium chloride (TEBAC) (Wang et al., 2006, 2005) (Scheme 35).

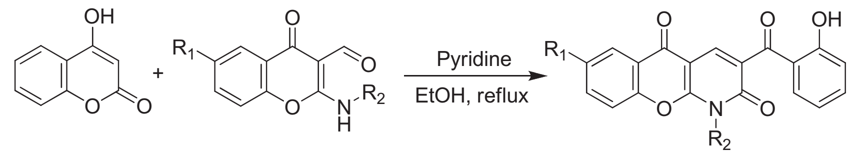
3.2.5. *Pyrano benzopyrans*

Pyrano[3,2-c]chromen-5-one (pyrano[3,2-c]coumarin) is the core of important natural products and heterocyclic structures. Molecules with such a nucleus exhibit a wide range of biological and pharmacological properties, such as antioxidant, anticancer, anti-inflammatory, antiviral, and antibacterial activities (Ahadi et al., 2013; Banard et al., 2002; Ghandi et al., 2013; Magiatis et al., 1998; Mahdavinia and Peikarporsan, 2013; Mail et al., 2002; Shafiee et al., 2011; Siddiqui, 2014). Many naturally occurring compounds with pyrano[3,2-c]coumarin skeletons have been isolated, such as isoethuliacoumarin A, isoethuliacoumarin B, isoethuliacoumarin C, ethuliacoumarin A, ethuliacoumarin B, and pterophyllin. In addition, pyrano[3,2-c]coumarin derivatives are also used as novel photochromers with promising applications in many photonic materials (Huang et al., 2007).

3.2.5.1. *2H,5H-pyrano[3,2-c]benzo[b]pyran-2,5-dione*. Many methods for the synthesis of 2*H*, 5*H*-pyrano[3,2-c]benzo[b]pyran-2,5-dione derivatives have been reported successively.

3.2.5.1.1. *Using alkyl-2-substituted-3-dimethyl-amino-propenoates*. Jakse et al. (2004) observed that the treatment of ethyl (2*E*)-3-dimethylamino-2-(1*H*-indol-3-yl)-propenoate **73** with **1** in acetic acid under reflux afforded 3-(1*H*-indol-3-yl)-2H,5*H*-pyrano[3,2-c]chromene-2,5-dione **74** (Scheme 36).

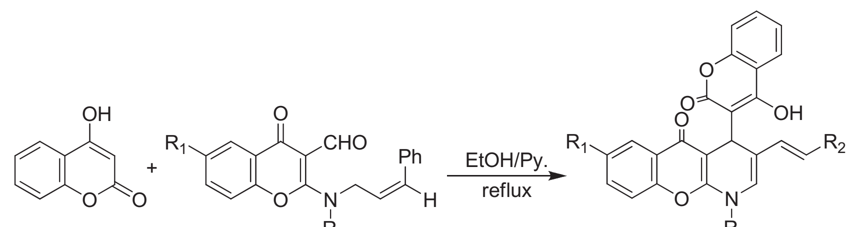
There are several reports in the literatures (Jukic et al., 2001a, 2001b; Sorsak et al., 1998; Toplak et al., 1997) about



1 **62** **63**

62,63	R_1	R_2	t / h	Yield%
a	Me	Ph	5	85
b	H	Ph	6	79
c	H	Et	5.5	79

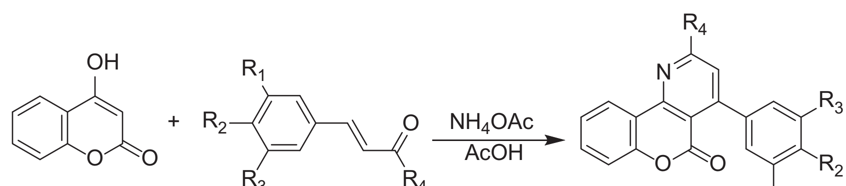
Scheme 31



1 **64** **65**

64,65	R_1	R_2	t / h	Yield%
a	H	$4\text{-}MeC_6H_4$	5	80
b	Me	Ph	4.5	76

Scheme 32

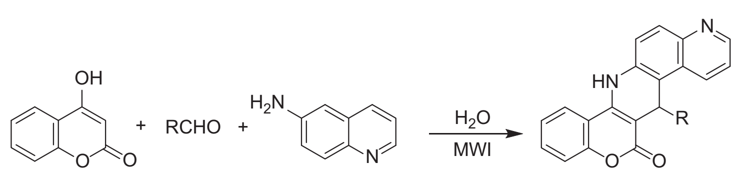


1 **66** **67** (30-62%)

R_1, R_2, R_3 = H, OCH_3

R_4 = H, 4-MeOPh

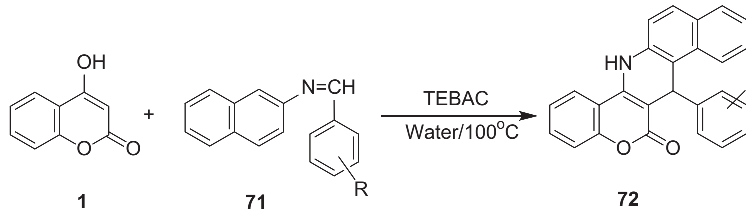
Scheme 33



1 **68** **69** **70**

68,70	a	b	c	d	e	f	g	h	i	j
R	$4\text{-}FC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}BrC_6H_4$	$4\text{-}CH_3OC_6H_4$	$4\text{-}NO_2C_6H_4$	$3\text{-}NO_2C_6H_4$	$4\text{-}CH_3C_6H_4$	C_6H_5	$2,4\text{-}Cl_2C_6H_3$	thien-2-yl
Conditions (time, yield)	(6min,93%)	(6min,93%)	(5min,94%)	(6min,95%)	(5min,94%)	(5min,95%)	(5min,95%)	(5min,94%)	(6min,93%)	(5min,95%)

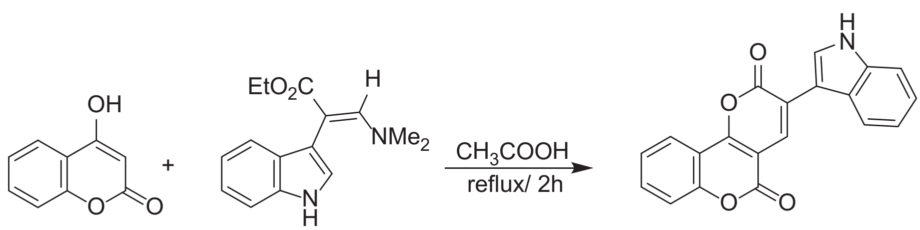
Scheme 34



1 **71** **72**

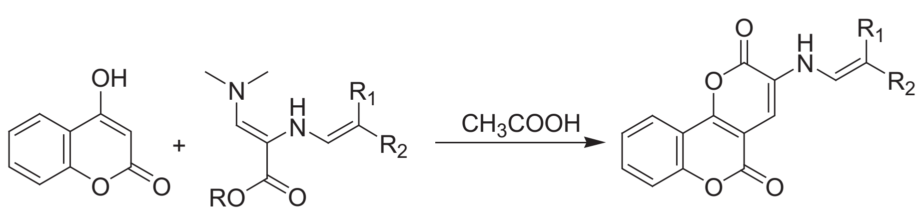
71,72	a	b	c	d	e	f	g	h	i	j	k	l
R	2-Br	2-Cl	3-Cl	4-Cl	2,4-Cl_2	3,4-Cl_2	4-OH	4-$(CH_3)_2N$	2-NO_2	4-CH_3O	3,4-$(CH_3)_2$	3,4-$(CH_3O)_2$
Time/ h	8	12	12	12	10	10	12	12	8	10	10	8
Yield %	93.3	94.0	90.2	87.8	90.9	95.0	92.3	95.2	90.5	92.7	95.0	88.9

Scheme 35



1 **73** **74** (73%)

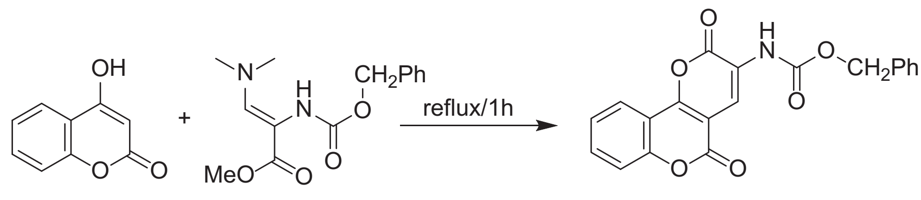
Scheme 36



1 **75** **76**

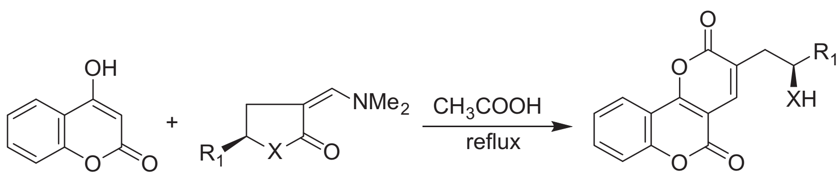
75,76	R	R_1	R_2	Yield%
a	Me	CO_2Et	Pyr	30
b	Et	CO_2Et	Pyr	30
c	Me	CN	Pyr	47
d	Et	CN	Pyr	58
e	CO_2Et	CO_2Ph	CO_2Ph	93
f	CO_2Et	CO_2Et	CO_2Et	41

Scheme 37



1 **77** **78** (59%)

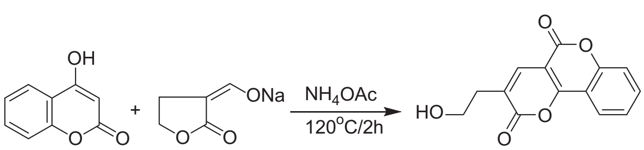
Scheme 38



1 **79** **80**

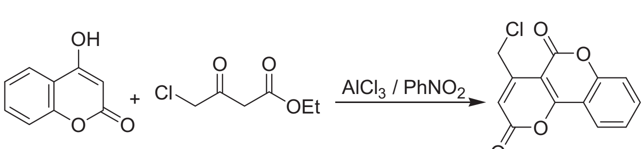
79,80	R_1	X	t/h	Yield%
a	CO_2Me	O	2	81
b	CO_2Me	N-COPh	2	93
c	CH_2CO_2Ph	O	3	37

Scheme 39



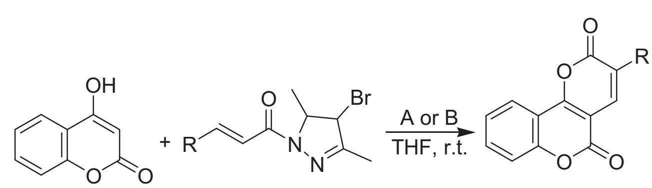
1 **81** **82** (81%)

Scheme 40



1 **83** **84** (69%)

Scheme 41



1 **85** **86**

85,86	R	t/min (A / B)	Yield % (A/B)
a	Me	2.5/3	66/81
b	Ph	144/48	64/85
c	4-Br-Ph	96/48	65/ 83
d	5-Br-Ph	168/---	53/---
e	3,5-Br_2-Ph	24/48	80/41
f	2-MeO-5-Br-Ph	---/144	---/ 76

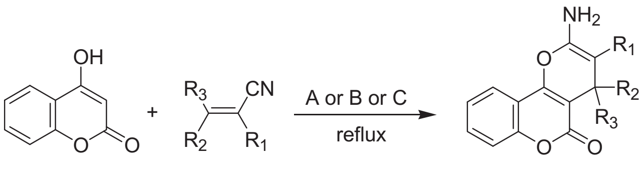
A : R,R-DBFOX/Ph+ $Ni(ClO_4)_2 \cdot 6H_2O$ + TMP
B : R,R-DBFOX/Ph+ $Ni(ClO_4)_2 \cdot 6H_2O$ + TMP+ Ac_2O

Scheme 42

the reaction of alkyl 2-[(2,2-disubstituted) ethenyl]amino-3-(dimethylamino)propenoate **75** with **1** in acetic acid for preparation of corresponding 2*H*,5*H*-pyrano[3,2-c]benzo[b]pyran-2,5-dione derivatives **76** (Scheme 37).

In 1999, it has been reported that the preparation of 3-(benzyloxycarbonyl)amino-2*H*,5*H*-pyrano[3,2-c]benzopyran-2,5-dione **78** was accomplished by the treatment of methyl-2-(benzyloxy carbonyl)amino-3-dimethylaminopropenoate **77** with **1** under reflux (Toplak et al., 1999) (Scheme 38).

3.2.5.1.2. Using substituted-tetrahydrofuran-2-one or oxopyrrolidine. A unique one step "ring switching" synthesis of (*S*)-3-(2,5-dioxo-2*H*,5*H*-benzo[b]pyrano[4,3,-b]pyran-3-yl)ester **80**



1 87 88

87,88	R_1	R_2	R_3	Yield % (Condition)
a	CN	Me	Me	60 (A)
b	CN	Naph.	H	85 (A)
c	NO_2	2-MeOC_6H_4	H	80 (B)
d	NO_2	3,4MeOC_6H_4	H	80 (B)
e	NO_2	4-MeOC_6H_4	H	85 (B)
f	CO_2Me	4-MeOC_6H_4	H	66 (C)
g	CN	4-MeOC_6H_4	H	52 (C)

A : Morphline /EtOH
B : TEA /EtOH
C : NaOMe/MeOH

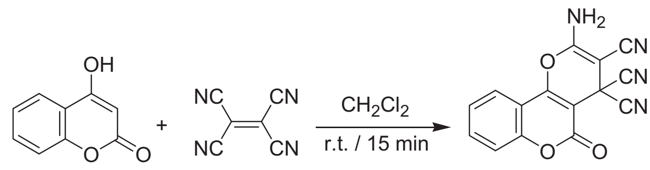
Scheme 43

is notable when **79** is reacted with **1** in boiling acetic acid (Mihelic et al., 2001) (Scheme 39).

An elegant, efficient one-pot synthesis of 3-hydroxyethyl-2-pyrano[3,2-c]benzopyran-2,5(6*H*)-dione **82** was achieved by the condensation of **1** with the sodium salt of α-formyl-γ-butyrolactone **81** in the presence of ammonium acetate (Toche et al., 1999) (Scheme 40).

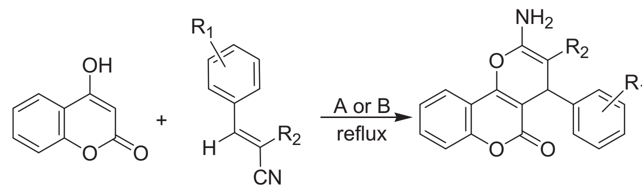
3.2.5.1.3. Using Pechmann-Duisberg reaction. The Pechmann-Duisberg reaction was employed by Abd El-Aziz et al. (2007) to synthesis 3-(chloromethyl)-2*H*-benzo[h]chromen-2-one **84** *via* condensation of **1** with ethyl 4-chloroacetoacetate **83** in the presence of nitrobenzene and anhydrous aluminum chloride (Scheme 41).

3.2.5.1.4. Using double catalytic activation conditions. Japanese research group presented an effective enantioselective synthetic method based on a concept of double catalytic activation by the use of catalytic amounts of chiral Lewis acid



1 91 **92** (84%)

Scheme 45



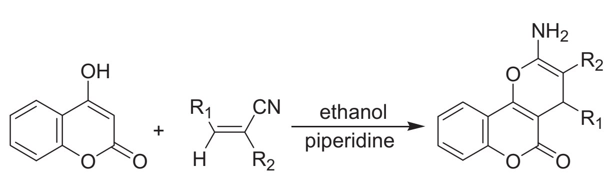
1 93 94

93,94	R_1	R_2	Time/h (A/B)	Yield% (A/B)
a	3-NO_2	CN	10 / 11	88 / 91
b	4-F	CN	10 / 8	93 / 93
c	3,4-$(CH_3O)_2$	CN	10 / 10	89 / 84
d	4-CH_3	CN	8 / 10	73 / 80
e	H	CO_2Et	8 / 8	90 / 85
f	4-F	CO_2Et	6 / 7	89 / 90
g	4-CH_3	CO_2Et	7 / 11	93 / 70
h	4-Cl	CO_2Et	7/ 7	97 / 80

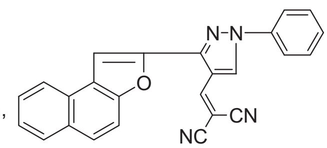
A : H_2O, TEBA, 90 °C.
B : KF-montmorillonite, DMF.

Scheme 46

and amine base, respectively. Thus, under the reaction conditions using 2,2,6,6-tetramethylpiperidine (TMP) and the enantio pure complex catalyst derived from the *R,R*-DBFOX/Ph ligand and nickel(II) perchlorate hexahydrate, the reaction of

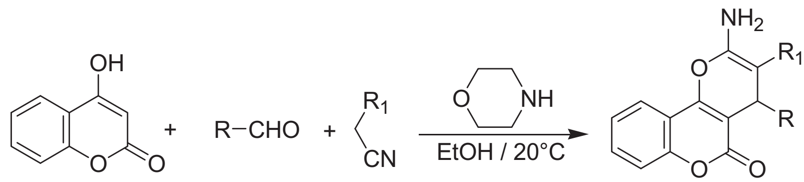


1 89 90

R_1: Ph, 4-NO_2-Ph, 4-Br-Ph, 4-Cl-Ph, 4-MePh, 4-MeO-Ph, 

R_2: CN , CO_2Et

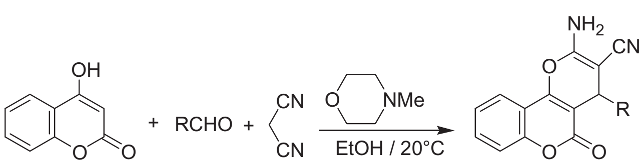
Scheme 44



1 56 95 96

56,95,96	R	R_1	Yield %
a	Me	CN	92
b	$Me(CH_2)_{10}$	CN	90
c	$Me(CH_2)_5$	CN	89
d	EtCH(Me)	CN	87
e	$Me(CH_2)_8$	CN	88
f	$CH(CH_3)_2$	NH_2-CS	74

Scheme 47



1 56 95 96

56,96	R	Yield %
a	i-Pr	80
b	$PhCH_2$	77
c	cyclohexyl	66
d	heptyl	59
e	cyclohex-3-enyi	90
f	i-Bu	87
g	$Ph(CH_2)_2$	61

Scheme 48

1 with 4-bromo-1-crotonoyl-3,5-dimethylpyrazole **85** in tetrahydrofuran at room temperature in the presence of acetic anhydride (Itoh and Kanemasa, 2003) or the absence of it (Itoh et al., 2005), to give the corresponding enol lactones in a good yield (Scheme 42).

3.2.5.2. Synthesis of amino-substituted pyranopyranones. Amino-substituted pyranopyranones are useful intermediates for the synthesis of bioactive natural products and pharmaceutical drugs (Dekamin et al., 2013; Jaggavarapu et al., 2014; Khan et al., 2014, 2011; Mehrabi and Abusaidi, 2010; Niknam and Jamali, 2012; Pansuriya et al., 2009; Prasanna and Raju, 2011; Shaabani et al., 2007; Shaterian and Oveisi, 2011; Tabatabaeian et al., 2012; Wang et al., 2010; Zheng and Li, 2011).

3.2.5.2.1. Two-component condensation. A number of publications have been taken out for Michael reactions **1** with a variety of substituted cinnamonitrile **87** in the presence of bases such as morpholine (Dyachenko and Rusanov, 2006; Kislyi et al., 1999), triethylamine (Mahmoud et al., 2009), sodium methoxide (Nesterov et al., 2005) resulted in the corresponding 2-aminopyrano[3,2-c]chromenes **88** (Scheme 43).

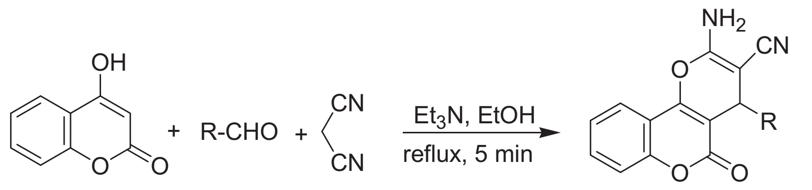
In a similar fashion, it was noted that Michael cycloaddition reaction of **1** with various substituted α-cyanocinnamonitriles **89** in ethanolic piperidine under reflux afforded pyrano[3,2-c]coumarins **90** (Bedair et al., 2000; El-Agrody et al., 2000; Abd El-Wahab et al., 2011) (Scheme 44).

Shaabani et al. (2008) described an isocyanide-catalyzed reaction between tetracyanoethylene **91** and **1** to afford 2-amino-5-oxopyrano[3,2-c]chromene-3,4,4(5*H*)-tricarbonitrile **92** in high yield at room temperature (Scheme 45).

The conversion of substituted cinnamonitriles **93** and **1** into 2-amino-4-aryl-4*H*,5*H*-pyrano[3,2-c][1]benzopyran-5-one derivatives **94** can be efficiently performed in water as a solvent using a catalytic amount of triethyl-benzylammonium chloride (TEBA) (Wang et al., 2004) or KF-montmorillonite (Tu et al., 2004) (Scheme 46).

3.2.5.2.2. Three component condensation.

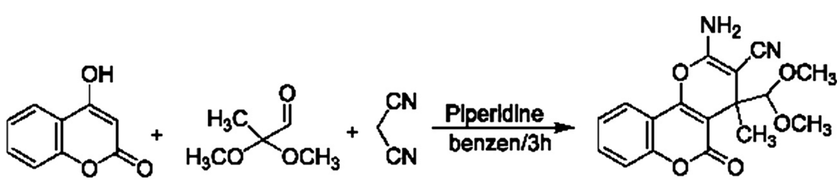
3.2.5.2.2.1. Conventional synthesis. The Knoevenagel cyclocondensation of aliphatic aldehyde **56** with malononitrile **95** and **1** in ethanol at 20 °C in the presence of morpholine yielded the corresponding derivatives of 4-alkyl(cycloalkyl)-2-amino-3-cyano-4*H*-pyran **96** which are potential biologically active compounds. Their analogs are used in the treatment of cardiovascular diseases and CNS disorders, as well as for the protection



1 56 95 96

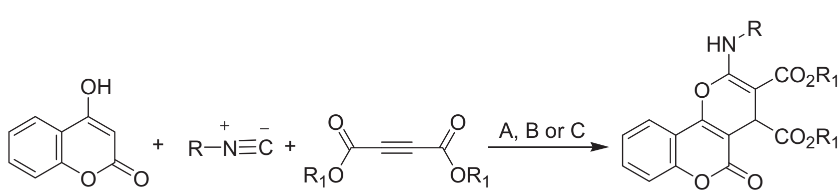
56,96	Ar	Yield %
a	4-Py	78
b	2-(5-$CH_3C_4H_2O$)	68
c	4-iPrO-C_6H_4	90
d	3-CH_3O-4-iPrOC_6H_3	74
e	3-CH_3O-4-(OCH_2CONH_2)C_6H_3	93

Scheme 49



1 97 95 98 (92%)

Scheme 50

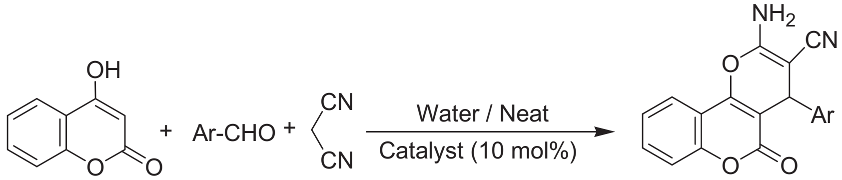


1 98 99 100

98,99,100	R	R_1	Yield% (A/B/C)
a	Me	tert-Butyl	88/93/-
b	Me	Cyclohexyl	78/68/97
c	Et	Cyclohexyl	90/--/90

A : CH_2Cl_2 , r.t , 24 h
B : Benzene, 80 °C, 5-6 h
C : Acetone , r.t .

Scheme 51

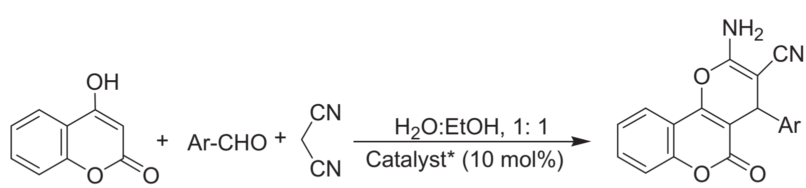


1 56 95 101

56,101	Ar	Time/min (A/B/C)	Yield% (A/B/C)
a	-Ph	7/8/45	92/92/91
b	4-MeO-Ph	10/10/60	/89/85
c	4-NO_2-Ph	5/5/45	86/96/86
d	2,4-Cl-Ph	8/15/50	88/95/87
e	4-Cl-Ph	30/5/5/45	94/97/93
f	4-OH-Ph	12/30/60	91/90/85
g	4-Br-Ph	5/5/50	94/93/91
h	4-F-Ph	5/5/60	84/96/84
i	4-Me-Ph	8/8/60	88/90/85

Catalyst:
A : 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).
B : 1-Butyl-3-methyl imidazolium hydroxide ([bmim]OH).
C : Tetrabutylammonium bromide (TBAB).

Scheme 52

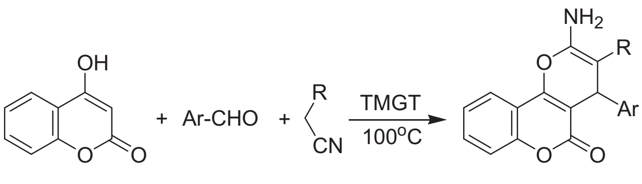


1 56 95 101

56,102	Ar	Time/min (A/B/C/D)	Yield% (A/B/C/D)
a	-Ph	240/180/32/30	81/72/89/89
b	4-MeO-Ph	240/180/35/50	80/73/87/80
c	3-NO_2-Ph	240/180/30/45	93/88/91/80
d	4-NO_2-Ph	240/180/30/85	95/82/92/85
e	2,4-Cl-Ph	240/180/30/75	90/75/92/75
f	4-Cl-Ph	240/180/30/75	85/78/91/75

Catalyst:
A: Diammonium hydrogen phosphate (DAHP), r.t.
B: (S)-proline, reflux.
C: Magnesium oxide (MgO), reflux with stirring.
D: $H_6P_2W_{18}O_{62}.18H_2O$, reflux.

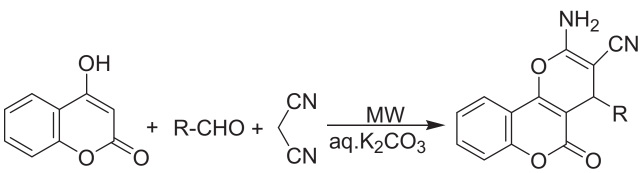
Scheme 53



1 56 95 101

56,101	Ar	R	t/min	Yield%
a	-Ph	CN	60	79
b	4-NO_2-Ph	CN	25	81
c	4-MeO-Ph	CN	50	70
d	4-NO_2-Ph	COOEt	50	82

Scheme 54



1 56 95 101

56,101	R	t/min	Yield %
a	phenyl	2.6	91
b	4-clorophenyl	2.8	89
c	2-furyl	2.0	92
d	3-indoly	2,2	93
e	piperonyl ,	2,5	88
f	2-chloro-3-quinolyl	1.8	87

Scheme 55

of crops from herbicide damage (Dyachenko and Chernega, 2006; Dyachenko, 2005) (Scheme 47).

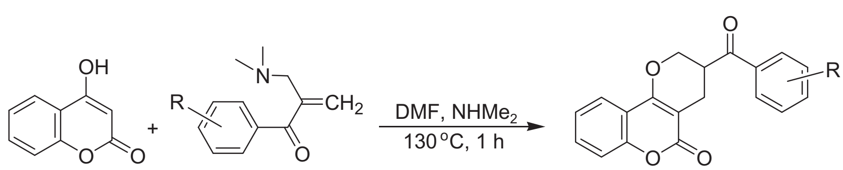
Klokol et al. (1999) described three component condensation of an aliphatic aldehyde **56** with malononitrile **95** and **1** at 20 °C in ethanol containing an equimolar amount of *N*-methylmorpholine led to the formation of the corresponding derivatives of 4-alkyl(cycloalkyl)-2-amino-3-cyano-4*H*-pyrans **96** (Scheme 48).

Shestopalov et al. (2005) noted that reaction of **1** with aromatic aldehyde **56** and malononitrile **95** in boiling ethanol in the presence of triethylamine as a catalyst gave substituted 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromenes **96** in high yields (68–93%) (Scheme 49).

Okamoto et al. (1997, 1996) investigated that a reaction of **1**, pyruvaldehyde dimethyl acetal **97** and malononitrile **95** in boiling benzene containing piperidine gave 2-amino-3-cyano-4-dimethoxymethyl-4-methyl-5-oxo-4*H*,5*H*-pyrano[3,2-c] chromene **98** in 92% yield (Scheme 50).

The one-pot three-component chemoselective condensation reaction of substituted isocyanides **98** with stoichiometric amount of dialkyl acetylenedicarboxylates **99** in the presence of **1** proceeded spontaneously under different conditions led to a facile synthesis of highly functionalized corresponding dialkyl-2-(alkylamino)-5-oxo-4*H*,5*H*-pyrano-[4,3-b] pyran-3,4-dicarboxylates **100**, in moderate to good yields (68–97%) (Cravotto et al., 2011; Sarma et al., 2010; Tietze et al., 2001; Yavari et al., 2008) (Scheme 51).

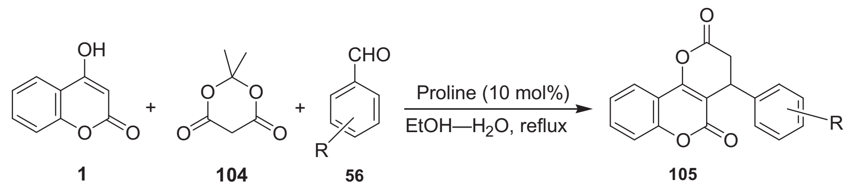
3.2.5.2.2.2. Using water. The one-pot, three-component reaction of diversely substituted aromatic aldehydes **56** with malononitrile **95** and **1** in water under reflux in the presence of a catalyst (DBU, ([bmim]OH), TBAB, titanium dioxide, sodium tungstate or spinel zinc ferrite) gave, in all cases, the corresponding dihydropyrano[c]chromenes **102** in good to excellent yields (Das et al., 2014; Gong et al., 2009; Khodabakhshi and Baghernejad, 2014; Khodabakhshi et al., 2014; Khurana et al., 2010; Khurana and Kumar, 2009) (Scheme 52). It is worthwhile to note that the reaction is faster with aldehydes having electron-withdrawing groups (such as nitro group and halide) than that with electron-donating groups (such as methoxyl group and hydroxyl group).



1 102 103

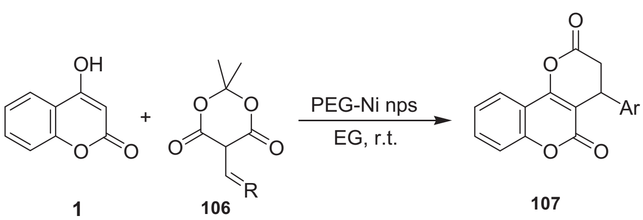
102,103	R	Yield %
a	H	78
b	Me	73
c	4-Br	82
d	2-Me	63
e	3,4-Cl_2	73
f	3,4$(OMe)_2$	70

Scheme 56



56,105	a	b	c	d	e	f	h
R	H	2-Br	3-Me	3-OMe	3-Cl	4-Cl	4-Me
Yield %	94	92	85	83	78	75	81

Scheme 57



106,107	Ar	t/min	Yield%
a	4-$CH_3OC_6H_4$	10	92
b	Piperonyl	7	89
c	2,5-$(CH_3O)_2C_6H_3$	10	91
d	4-ClC_6H_4	15	78

Scheme 58

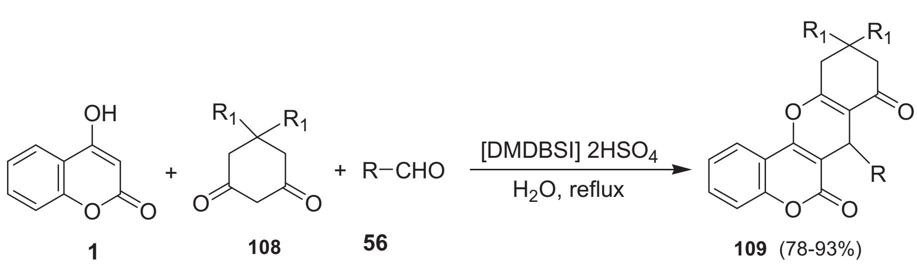
Heravi et al. (2008) demonstrated an elegant protocol and eco-friendly route to the synthesis of 2-amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitriles **101** *via* a three component reaction of aryl aldehydes **56**, malononitrile **95** and **1** using $H_6P_2W_{18}O_{62}$ .18H_2O, which proceeds efficiently in aqueous ethanol under heating conditions. Many catalysts (DAHP or (S)-proline (Abdolmohammadi and Balalaie, 2007) or MgO (Seifi and Sheibani, 2008) or $FeNi_3$–SiO_2 (Nasseri and Sadeghzadeh, 2013)) have also been used as another catalysts for this reaction (Scheme 53). Recently, Yao et al. (2013) found that 2-amino-4-aryl-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitriles **101** could be prepared without catalyst in a mixed solvent of ethanol and water.

3.2.5.2.2.3. Using ionic liquid. 1,1,3,3-*N,N,N′,N′*-Tetramethylguanidinium trifluoroacetate (TMGT) as an ionic liquid, efficiently promoted one-pot, three-component condensation of aldehydes **56**, alkylnitriles **95** and **1** afforded pyran annulated heterocyclic systems **101** (Shaabani et al., 2005a) (Scheme 54).

3.2.5.2.2.4. Microwave irradiation. Kidwai and Saxena (2006) exploited an easier, practically convenient, novel, ecologically safe method for the synthesis of pyrano[3,2-c]benzopyran (R = phenyl, 4-chlorophenyl, 2-furyl, 3-indoly, piperonyl, 2-chloro-3-quinolyl) **101** by three-component reaction of aldehyde **56**, malononitrile **95** and **1** in aqueous K_2CO_3 as a green catalyst under microwave heating. The observed yields and enhancement in reaction rates can be attributed to the uniform heating effect of microwave (Scheme 55).

3.2.6. 3,4-Dihydro-2H,5H-1-benzopyrano[4,3-b]pyran-5-one

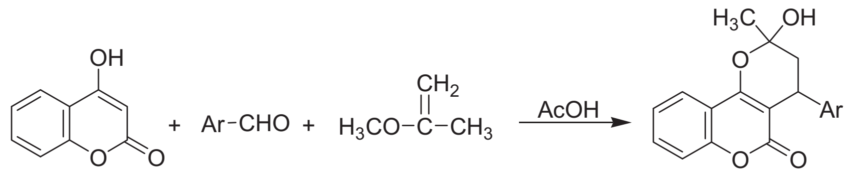
Treatment of **1** with 1-aryl-2-[(dimethylamino)methyl]-2-propen-1-ones **102** in dimethylformamide in the presence of a catalytic amount of dimethylamine under reflux conditions afforded 3-benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-b]pyran-5-ones **103** (Girreser et al., 1998) (Scheme 56).



R : Ph Me , 2-ClC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 3-OHC_6H_4 , 3-$NO_2C_6H_4$, 4-$MeOC_6H_4$,4-ClC_6H_4,4-$NO_2C_6H_4$, 3,4-$(Me)_2C_6H_3$, 2-F-6-ClC_6H_3, 2,4-$(Cl)_2C_6H_3$, 3-MeO-4-OHC_6H_3 , Furan-2-yl , Thiophene-2-yl , CH_3CH_2 , $CH_3CH_2CH_2$

R_1 : H, Me

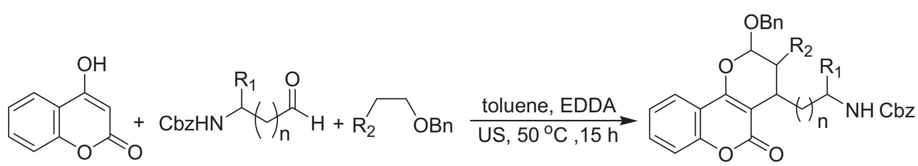
Scheme 59



1 110 111 112

110,112	Ar	Yield %
a	Ph	83
b	4-Cl-C_6H_4	74
c	4-NO_2-C_6H_4	70
d	furyl	68

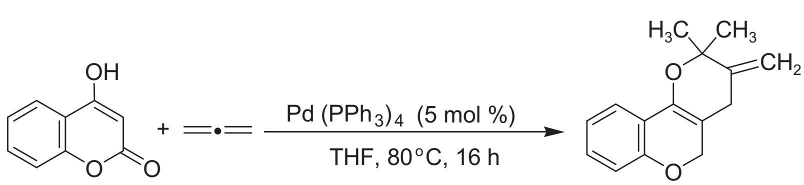
Scheme 60



1 113 114 115

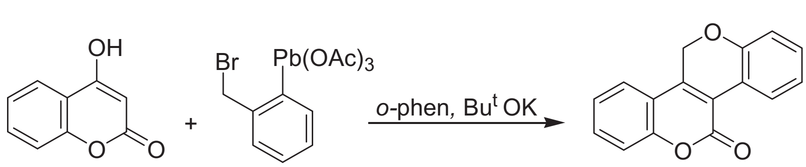
n : 0,1,2 **R_1** : iPr, iBu, Bn, Me **R_2** : iPr, Et, Me, H
Cbz : benzyloxycarbonyl **Bn** : Benzyl.

Scheme 61



1 116 **117** (34%)

Scheme 62

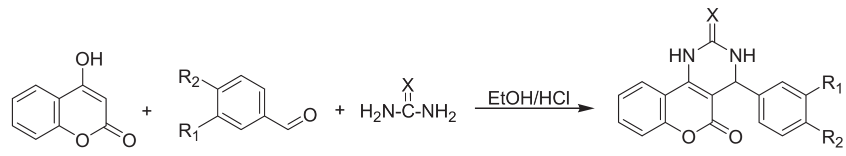


1 118 **119** (76%)

Scheme 63

Proline-promoted efficient enantioselective synthesis of 4-aryl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-c]chromene-2,5-diones **105** from **1**, Meldrum's acid **104**, and benzaldehydes **56** (Yavari et al., 2008) (Scheme 57). The functionalized chromenes reported in this work may be considered as potentially useful synthetic intermediates because they possess atoms with different oxidation states.

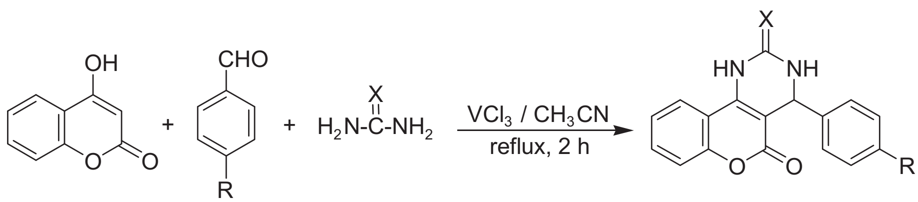
Khurana and Vij (2011) reported that the reaction of 5-arylidene Meldrum's acids **106** with **1** in the presence PEG-stabilized Ni nanoparticles underwent rapid and tandem



1 56 120 121

R_1 = H, OMe; R_2 = H, Me, OMe; X = O, S

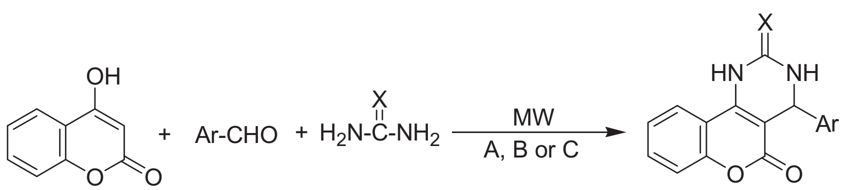
Scheme 64



1 56 120 122 (75-86%)

R = H, Cl, F, OH **X** = O,S

Scheme 65



1 56 120 123

120,123	Ar	X	t /Sec. (A/B/C)	Yield% (A/B/C)
a	4-ClC_6H_4	O	100/60/100	83/90/85
b	4-ClC_6H_4	S	110/65/100	80/92/82
c	3-Furyl	O	100/75/85	82/95/84
d	3-Furyl	S	120/70/95	79/92/80
e	$4\text{-N(CH}_3)_2C_6H_4$	O	115/75/100	80/89/82
f	$4\text{-N(CH}_3)_2C_6H_4$	S	110/60/105	81/93/85
g	3-Indolyl	O	110/65/100	82/92/83
h	3-Indolyl	S	120/70/90	80/90/85
i	$3\text{-NO}_2C_6H_4$	O	100/65/85	75/93/80
j	$3\text{-NO}_2C_6H_4$	S	105/60/95	79/90/85

A : Silica gel
B : Montmorillonite
C : Acidic alumina.

Scheme 66

enol lactonization involving Michael addition to give 4-aryl-3,4-dihydropyrano[3,2-c]chromene-2,5-diones **107** (Scheme 58).

Three-component cyclocondensation of **1**, aldehydes **56**, and cyclic 1,3-dicarbonyl compounds **108** were prompted by ionic liquids 1,3-dimethyl-2-oxo-1,3-bis(4-sulfobutyl)imidazolidine-1,3-diium hydrogen sulfate ([DMDBSI].2HSO_4) in water to provide a novel series of 10,11-dihydro-chromeno[4,3-b]chromene-6,8(7*H*,9*H*)-dione derivatives **109** (Chen et al., 2011) (Scheme 59). Also, this reaction can be achieved using a catalytic amount of heteropolyacids or molecular iodine (Motamedi et al., 2012; Sun et al., 2012).

Cravotto et al. (2011) have disclosed a distinct improvement in the synthesis of pyranocoumarin derivatives through a pericyclic approach. This route offers a valid alternative to the standard industrial synthesis for 3,4-dihydropyranocoumarins **112** were obtained by a hetero Diels–Alder (HDA) with inverse electron demand between **1**, aromatic aldehydes **110** (such as benzaldehyde, 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, and 2-furancarboxaldehyde) and electron-rich alkenes **111** (Scheme 60).

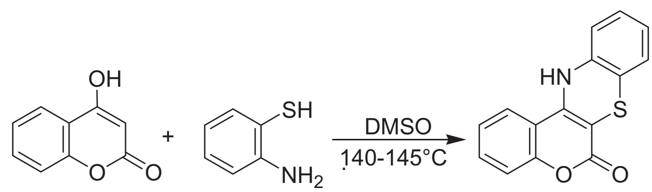
Tietze et al. (2001) concluded that a multicomponent domino Knoevenagel/hetero-Diels–Alder reaction of **1** with an amino aldehyde **113** and benzyl enol ethers **114**, in toluene in the presence of catalytic amounts of ethylenediammonium diacetate (EDDA) and trimethyl orthoformate as dehydrating agent in an ultrasonic bath at 50 °C affords a benzyl-protected acetal **115** (Scheme 61).

Reaction of **1** with allene **116** in tetrahydrofuran in the presence of tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] afforded 3,4-dihydro-2,2-dimethyl-3-methylenepyrano[3,2-c]chromen-5(2*H*)-one **117** (Grigg et al., 2001) (Scheme 62).

3.2.7.4. 6H,11H-[2]Benzopyrano[4,3-c][1]benzopyran-11-one. The reaction of 2-(bromomethyl)phenyllead triacetate **118** with **1** carried out in the presence of a combination of *o*-phenanthroline-potassium *t*-butoxide (3:1) as a base for reductive coupling gave 6*H*,11*H*-[2]benzopyrano[4,3-c][1]benzopyran-11-one **119** (Ganina et al., 2005; Naumov et al., 2005) (Scheme 63).

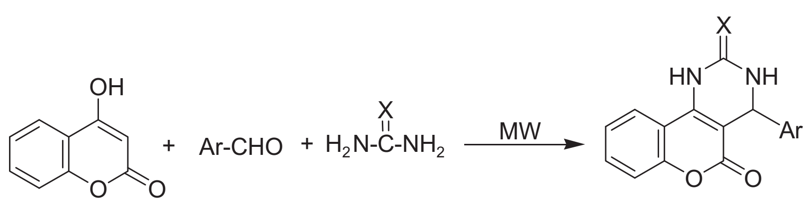
3.2.8. Benzopyrano[4,3-d]pyrimidines

3.2.8.1. Using conventional heating. 4-Aryl-1,2,3,4-tetrahydrobenzopyrano[4,3-d]pyrimidine-2,5-diones/pyrimidine-thione-5-ones **121** were prepared by reacting **1** with aromatic aldehydes **56** and urea/thiourea **120** in ethanol in the presence of concentrated hydrochloric acid, but this procedure requires prolonged heating of the reaction mixture and tedious workup



1 **125** **126**

Scheme 68



1 **56** **120** **124**

56, 120,124	X	Ar	t /min.	Yield %
a	O	Ph	2.6	94
b	S	Ph	22	92
c	O	3-indolyl	2.9	90
e	S	3-indolyl	3.1	88
f	O	1,3-2H-benzo dioxol-5-yl	3.3	93
g	S	1,3-2H-benzo dioxol-5-yl	3.4	95
h	O	2-chloroquin -olin-3-yl	4.1	86
i	S	2-chloroquin -olin-3-yl	4.3	87

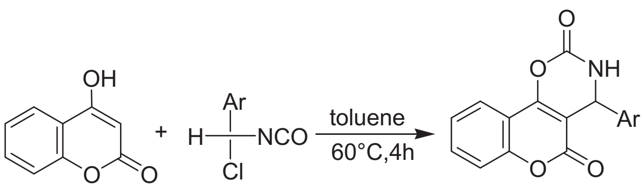
Scheme 67

and gives low yields of the products (Brahmbhatt et al., 1999) (Scheme 64).

3.2.8.2. Solution phase synthesis. Due to short reaction times, high yields and easy work-up procedures combined with the use of the multiple synthesizer, Sabitha et al. (2003) found that three component condensation of **1,** an aromatic aldehyde **56**, and urea (thiourea) **120** in refluxing acetonitrile containing a catalytic amount of VCl_3 gave the dihydropyrimidinones **122** with high purity >95%. (Scheme 65).

3.2.8.3. Microwave irradiation. Acidic solid support coupled with microwave is an appropriate method for the synthesis of 4-substituted benzopyrano[4,3-d]pyrimidine derivatives **123** in a few seconds with improved yield as compared to conventional heating. The main advantage being that solid supports do not absorb microwaves at 2450 MHz, so are not an obstacle for the transition of microwaves to the reactants. In addition, the limitations of the MWI assisted reaction in solvents, namely, the development of high pressure and the need for specialized sealed vessels are circumvented via this solid state technique which enables organic reactions to occur rapidly at atmospheric pressure. Montmorillonite K10 clay is a better support as compared to silica gel and acidic alumina in terms of yield and time for the synthesis of benzopyranopyrimidines **123** (Kidwai and Sapra, 2002) (Scheme 66).

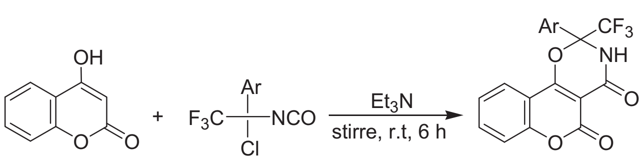
Kidwai et al. (2006) developed a highly efficient environmentally benign method is proposed for the synthesis of benzopyranopyrimidines **124** apart from acidic solid support by reaction of **1** with aldehydes **56** and urea or thiourea **120** in the absence of a solvent under microwave irradiation in a few minutes gave the desired products in 90–95% yields. The



1 **127** **128**

127,128	Ar	Yield %
a	Ph	75
b	2-FC_6H_4	67
c	4-$NO_2C_6H_4$	72

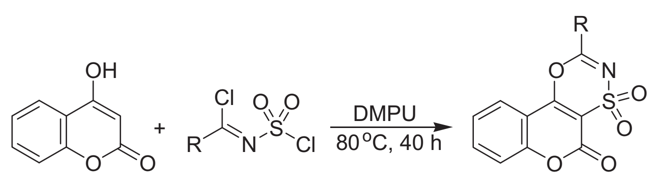
Scheme 69



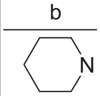
1 **129** **130**

129,130	Ar	Yield %
a	4-MeC_6H_4	75
b	4-$MeOC_6H_4$	71

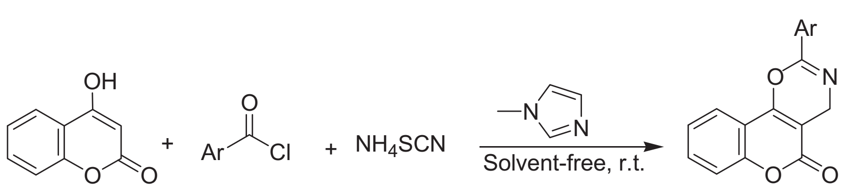
Scheme 70



1 **134** **135**

134,135	a	b
R		
Yield %	24	11

Scheme 72



1 **131** **132** **133**

131,133	a	b	c	d	e	f
Ar	Ph	4-Cl-Ph	4-Br-Ph	4-CH_3-Ph	3-NO_2-Ph	4-NO_2-Ph
Yield %	91	93	94	90	90	91

Scheme 71

proposed procedure utilizes neither solvents nor solid support nor acid catalyst, requires no special equipment, improves the product yield and shortens the reaction time and minimizes hazardous pollution (Scheme 67).

3.2.9. Benzopyranobenzothiazinones

One of the most successful strategies for constructing of 6,12-dihydro-1-benzopyrano[3,4-b][1,4]benzothiazin-6-one **126**, new agents with estrogenic activity mediated by estrogen receptors (ER), is the condensation and oxidative cyclization of substituted 2-aminobenzenethiol **125** with **1** in dimethyl sulfoxide at 140–150 °C (Aguirre-Pranzoni et al., 2011; Anary-Abbasinejad et al., 2008; Gupta et al., 2004; Gupta and Gupta, 2009) (Scheme 68).

3.2.10. Chromeno[3,4-e][1,3]oxazine

Vovk et al. (2007) have described the reaction of **1** with 1-chlorobenzyl isocyanates **127** occurred in anhydrous toluene at 60 °C, did not require the presence of an organic base, and led to the formation of 4-aryl-3,4-dihydro-2*H*,5*H*-chromeno[3,4-e][1,3]oxazine-2,5-diones **128** in 67–75% yields (Scheme 69).

However, 1-aryl-2,2,2-trifluoro-1-chloroethyl isocyanates **129** reacted with **1** in the presence of triethylamine in toluene gave 2-aryl-2-trifluoromethyl-2,3-dihydro-4*H*,5*H*-chromeno-[3,4-e][1,3]oxazine-4,5-diones **130** (Vovk et al., 2007) (Scheme 70).

Hassanabadi et al. (2011) concluded that the reaction of acid chlorides **131** and ammonium thiocyanate **132** with **1** in the presence of *N*-methylimidazole led to oxazine derivatives **133** in excellent yields. The present procedure has the advantage that the reaction is performed under neutral conditions and the starting material can be used without any activation or modification (Scheme 71).

3.2.11. Pyrano[3,4-e][1,4,3]oxathiazines

Cablewski et al. (2007) investigated the regioselective reaction of **1** with *N*,*N*-dialkyl-*N*′-chlorosulfonylchloro formamidines **134** in the presence of *N*,*N*′-dimethyl-*N*,*N*′-propylene urea (DMPU) afforded 3-dialkylamino-1,1,8-trioxo-1*H*-6-pyrano[3,4-e][1,4,3]oxathiazines **135** (Scheme 72).

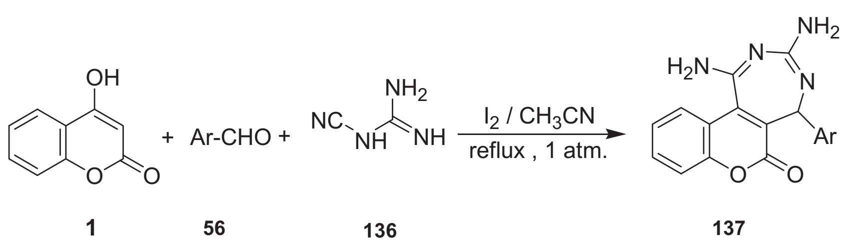
3.3. [7-6] Ring system

3.3.1. Benzopyrano[1,3]diazepines

Kidwai et al. (2007) have shown that a simple and facile synthesis of 7-arylbenzopyrano[1,3]diazepines **137** was accomplished by the treatment of **1**, aromatic/heteroaromatic aldehydes **56**, and cyanoguanidine **136** using molecular iodine as a novel catalyst in acetonitrile under reflux. This method not only provides an excellent complement to benzopyrano[1,3]diazepines **137** but also avoids the multistep and harsh reaction conditions (Scheme 73).

4. Conclusion

The present review is a summary of progress in 4-hydroxycoumarin as a versatile synthetic building block to the synthesis of all sorts of heterocycles or fused heterocycles. Even though a lot of progress has reported, We hope more astonishing applications of this compound will be revealed in the near future, and that this review may light a candle in organic chemistry.



56, 137	Ar	t/h	Yield%
a	C_6H_5	3.2	89
b	4-ClC_6H_4	2.8	91
c	3-$NO_2C_6H_4$	3.4	92
d	2-OHC_6H_4	4.8	85
e	4-$CH_3OC_6H_4$	4.0	93
f	–CH=CH–C_6H_4	1.5	96
g	3,4-Piperonyl	3.7	87
h	2-Thiophenyl	2.5	90

Scheme 73

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